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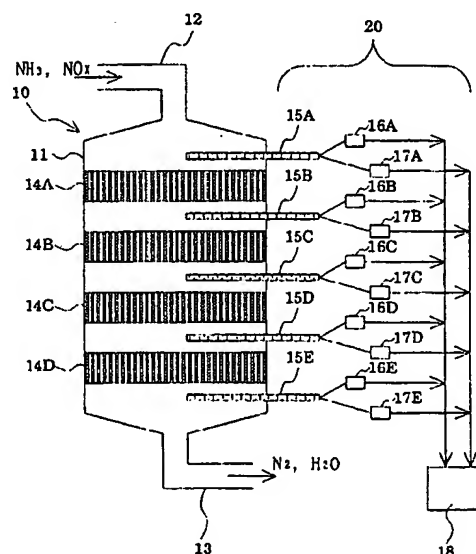
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(54) **APPARATUS FOR MONITORING NO<sub>x</sub> REMOVAL CATALYST OF DENITRIZER AND METHOD OF MONITORING NO<sub>x</sub> REMOVAL CATALYST**

(57) To provide an NO<sub>x</sub> removal catalyst management unit for use with an NO<sub>x</sub> removal apparatus, the management unit detecting an NO<sub>x</sub> removal catalyst layer that is actually deteriorated, whereby the deteriorated catalyst layer can be effectively replaced by a new catalyst layer, and to provide a method for managing the NO<sub>x</sub> removal catalyst.

The management unit for managing a plurality of NO<sub>x</sub> removal catalyst layers provided in a flue gas NO<sub>x</sub> removal apparatus includes NO<sub>x</sub> measurement means 16A through 16E for determining NO<sub>x</sub> concentrations on the inlet and outlet sides of respective NO<sub>x</sub> removal catalyst layers 14A through 14D; NH<sub>3</sub> measurement means 17A through 17E for determining NH<sub>3</sub> concentrations on the inlet and outlet sides of the same NO<sub>x</sub> removal catalyst layers; and percent NO<sub>x</sub> removal determination means 18 for determining percent NO<sub>x</sub> removal ( $\eta$ ) on the basis of an inlet mole ratio (i.e., inlet NH<sub>3</sub>/inlet NO<sub>x</sub>).

FIG. 1



EP 1 514 590 A1

**Description**

## Technical Field

5 [0001] The present invention relates to an NO<sub>x</sub> removal catalyst management unit for use with an NO<sub>x</sub> removal apparatus, the management unit being provided for carrying out performance management on an NO<sub>x</sub> removal catalyst included in a flue gas NO<sub>x</sub> removal apparatus installed in a facility such as a thermal power station, and to a method for managing the NO<sub>x</sub> removal catalyst.

## 10 Background art

[0002] Conventionally, boilers provided in thermal power stations and a variety of large-scale boilers employing a fuel such as petroleum, coal, or fuel gas, waste incinerators, and similar apparatuses have been equipped with a flue gas NO<sub>x</sub> removal apparatus which contains a plurality of NO<sub>x</sub> removal catalyst layers.

15 [0003] The above employed NO<sub>x</sub> removal catalysts assume the form of honeycomb, plate, etc. During use, the catalytic performance of the catalysts is problematically deteriorated with elapse of time as a result of deposition, on the surface of the catalyst, of a substance which deteriorates the catalytic performance (hereinafter referred to as deteriorating substance) or through migration of the dissolved deteriorating substance into the catalyst.

20 [0004] Conventionally, the performance of the NO<sub>x</sub> removal catalysts has been managed by measuring NO<sub>x</sub> concentration and unreacted NH<sub>3</sub> concentration on the inlet and outlet sides of respective catalysts. When a drop in total performance of a catalyst system is confirmed, old catalysts are replaced with new catalysts or regenerated catalysts in order of use age, and such replacement is carried out periodically.

[0005] Generally, NO<sub>x</sub> removal catalysts are very expensive. Thus, there has been proposed one approach for prolonging the service life of the NO<sub>x</sub> removal catalysts to as long a duration as possible by assessing the performance of each unit catalyst (Japanese Patent Publication (*kokoku*) No. 7-47108).

25 [0006] However, the aforementioned catalyst managing method has a drawback. According to the method, NO<sub>x</sub> concentration and unreacted NH<sub>3</sub> concentration of each catalyst layer are determined, and percent NO<sub>x</sub> removal and percent contribution of each catalyst layer are calculated from the determined NO<sub>x</sub> concentration. On the basis of these values, performance-deteriorated catalysts are replaced with new catalysts in order of degree of deterioration. In this case, when the catalytic performance is evaluated by the percent contribution calculated on the basis of the NO<sub>x</sub> concentration, the catalyst layer(s) having actually deteriorated performance cannot be detected correctly.

30 [0007] In view of the foregoing, an object of the present invention is to provide an NO<sub>x</sub> removal catalyst management unit for use with an NO<sub>x</sub> removal apparatus, the management unit detecting an NO<sub>x</sub> removal catalyst layer that is actually deteriorated, whereby the deteriorated NO<sub>x</sub> removal catalyst layer can be effectively replaced by a new catalyst layer. Another object of the invention is to provide a method for managing the NO<sub>x</sub> removal catalyst.

## Disclosure of the Invention

40 [0008] In order to attain the aforementioned objects, a first mode of the present invention provides an NO<sub>x</sub> removal catalyst management unit for use with an NO<sub>x</sub> removal apparatus, the management unit being provided for managing a plurality of NO<sub>x</sub> removal catalyst layers provided in a flue gas NO<sub>x</sub> removal apparatus, characterized in that the management unit comprises NO<sub>x</sub> measurement means for determining NO<sub>x</sub> concentrations on the inlet and outlet sides of respective NO<sub>x</sub> removal catalyst layers; NH<sub>3</sub> measurement means for determining NH<sub>3</sub> concentrations on the inlet and outlet sides of the same NO<sub>x</sub> removal catalyst layers; and percent NO<sub>x</sub> removal determination means for determining percent NO<sub>x</sub> removal ( $\eta$ ) on the basis of an inlet mole ratio (i.e., inlet NH<sub>3</sub>/inlet NO<sub>x</sub>).

45 [0009] According to the first mode, NO<sub>x</sub> concentrations and NH<sub>3</sub> concentrations are determined on the inlet and outlet sides of respective NO<sub>x</sub> removal catalyst layers, and the percent NO<sub>x</sub> removal ( $\eta$ ) is determined on the basis of an inlet mole ratio. Therefore, the percent NO<sub>x</sub> removal, which is enhanced as the mole ratio increases, can be evaluated on an absolute basis and correctly.

50 [0010] A second mode of the present invention is drawn to a specific embodiment of the NO<sub>x</sub> removal catalyst management unit of the first mode for use with an NO<sub>x</sub> removal apparatus, wherein the percent NO<sub>x</sub> removal ( $\eta$ ) is determined on the basis of NH<sub>3</sub> concentrations.

[0011] According to the second mode, the percent NO<sub>x</sub> removal ( $\eta$ ) of each and every NO<sub>x</sub> removal catalyst layer is determined on the basis of NH<sub>3</sub> concentrations rather than on the basis of NO<sub>x</sub> concentrations. Therefore, the catalytic performance can be detected with smaller variation.

55 [0012] A third mode of the present invention is drawn to a specific embodiment of the NO<sub>x</sub> removal catalyst management unit of the second mode for use with an NO<sub>x</sub> removal apparatus, wherein the percent NO<sub>x</sub> removal ( $\eta$ ) is determined on the basis of the following equation (1):

$$\eta = \{(\text{inlet NH}_3 - \text{outlet NH}_3)/(\text{inlet NH}_3 - \text{outlet NH}_3 + \text{outlet NO}_x)\} \times 100 \times (\text{evaluation mole ratio/inlet mole ratio}) \quad (1).$$

**[0013]** According to the third mode, the percent NO<sub>x</sub> removal (η) of respective NO<sub>x</sub> removal catalyst layers can be detected without variation and correctly, thereby managing respective NO<sub>x</sub> removal catalysts successfully and effectively.

**[0014]** A fourth mode of the present invention is drawn to a specific embodiment of the NO<sub>x</sub> removal catalyst management unit of any of the first to third modes for use with an NO<sub>x</sub> removal apparatus, which management unit further includes transmission means for transmitting concentration values determined by the NO<sub>x</sub> measurement means and the NH<sub>3</sub> measurement means to the percent NO<sub>x</sub> removal determination means, wherein the percent NO<sub>x</sub> removal determination means determines the percent NO<sub>x</sub> removal (η) of respective NO<sub>x</sub> removal catalyst layers included in a plurality of flue gas NO<sub>x</sub> removal apparatuses.

**[0015]** According to the fourth mode, NO<sub>x</sub> removal catalysts included in a plurality of flue gas NO<sub>x</sub> removal apparatuses can be collectively managed, thereby effectively managing NO<sub>x</sub> removal catalysts.

**[0016]** A fifth mode of the present invention provides a method for managing an NO<sub>x</sub> removal catalyst for use with an NO<sub>x</sub> removal apparatus, the method being provided for managing a plurality of NO<sub>x</sub> removal catalyst layers provided in a flue gas NO<sub>x</sub> removal apparatus, characterized in that the method comprises determining NO<sub>x</sub> concentrations and NH<sub>3</sub> concentrations on the inlet and outlet sides of respective NO<sub>x</sub> removal catalyst layers; determining percent NO<sub>x</sub> removal (η) on the basis of an inlet mole ratio (i.e., inlet NH<sub>3</sub>/inlet NO<sub>x</sub>); and evaluating performance of respective NO<sub>x</sub> removal catalyst layers on the basis of the percent NO<sub>x</sub> removal (η).

**[0017]** According to the fifth mode, NO<sub>x</sub> concentrations and NH<sub>3</sub> concentrations are determined on the inlet and outlet sides of respective NO<sub>x</sub> removal catalyst layers, and the percent NO<sub>x</sub> removal (η) is determined on the basis of an inlet mole ratio. Therefore, the percent NO<sub>x</sub> removal, which is enhanced as the mole ratio increases, can be evaluated on an absolute basis and correctly.

**[0018]** A sixth mode of the present invention is drawn to a specific embodiment of the method for managing an NO<sub>x</sub> removal catalyst of the fifth mode for use with an NO<sub>x</sub> removal apparatus, wherein the percent NO<sub>x</sub> removal (η) is determined on the basis of NH<sub>3</sub> concentrations.

**[0019]** According to the sixth mode, the percent NO<sub>x</sub> removal (η) of respective NO<sub>x</sub> removal catalyst layers is determined on the basis of NH<sub>3</sub> concentrations rather than on the basis of NO<sub>x</sub> concentrations. Therefore, the catalytic performance can be detected without variation.

**[0020]** A seventh mode of the present invention is drawn to a specific embodiment of the method for managing an NO<sub>x</sub> removal catalyst of the sixth mode for use with an NO<sub>x</sub> removal apparatus, wherein the percent NO<sub>x</sub> removal (η) is determined on the basis of the following equation (1):

$$\eta = \{(\text{inlet NH}_3 - \text{outlet NH}_3)/(\text{inlet NH}_3 - \text{outlet NH}_3 + \text{outlet NO}_x)\} \times 100 \times (\text{evaluation mole ratio/inlet mole ratio}) \quad (1).$$

**[0021]** According to the seventh mode, the percent NO<sub>x</sub> removal of each NO<sub>x</sub> removal catalyst layer can be detected without variation and correctly, thereby managing respective NO<sub>x</sub> removal catalysts successfully and effectively.

**[0022]** An eighth mode of the present invention is drawn to a specific embodiment of the method for managing an NO<sub>x</sub> removal catalyst of any of the fifth to seventh modes for use with an NO<sub>x</sub> removal apparatus, wherein the method further comprises performing restoration treatment of an NO<sub>x</sub> removal catalyst layer having a catalytic performance deteriorated to a predetermined level, on the basis of results of performance evaluation of the respective NO<sub>x</sub> removal catalyst layers.

**[0023]** According to the eighth mode, the percent NO<sub>x</sub> removal of each NO<sub>x</sub> removal catalyst layer is determined without variation and correctly, and the performance restoration treatment is carried out on the basis of the results. Thus, respective NO<sub>x</sub> removal catalysts can be effectively used.

**[0024]** A ninth mode of the present invention is drawn to a specific embodiment of the method for managing an NO<sub>x</sub> removal catalyst of the eighth mode for use with an NO<sub>x</sub> removal apparatus, wherein the performance restoration treatment is replacement of the NO<sub>x</sub> removal catalyst layer with a new NO<sub>x</sub> removal catalyst layer, replacement of the NO<sub>x</sub> removal catalyst layer with a regenerated NO<sub>x</sub> removal catalyst layer, replacement of the NO<sub>x</sub> removal catalyst layer with an NO<sub>x</sub> removal catalyst layer inverted with respect to the direction of the flow of discharge gas, or replacement of the NO<sub>x</sub> removal catalyst layer with an NO<sub>x</sub> removal catalyst layer from which a deteriorated portion has been

removed.

[0025] According to the ninth mode, the performance of deteriorated NO<sub>x</sub> removal catalysts can be restored through any of the above treatments.

[0026] A tenth mode of the present invention is drawn to a specific embodiment of the method for managing an NO<sub>x</sub> removal catalyst of any of the fifth to ninth modes for use with an NO<sub>x</sub> removal apparatus, wherein the method further comprises determining the percent NO<sub>x</sub> removal of respective NO<sub>x</sub> removal catalyst layers included in a plurality of flue gas NO<sub>x</sub> removal apparatuses and evaluating catalytic performance of respective NO<sub>x</sub> removal catalyst layers included in a plurality of flue gas NO<sub>x</sub> removal apparatuses.

[0027] According to the tenth mode, NO<sub>x</sub> removal catalysts included in a plurality of flue gas NO<sub>x</sub> removal apparatuses can be collectively managed, thereby effectively managing NO<sub>x</sub> removal catalysts.

[0028] As described hereinabove, the present invention employs an NO<sub>x</sub> removal catalyst management unit for use with an NO<sub>x</sub> removal apparatus, which management unit comprises NO<sub>x</sub> measurement means for determining NO<sub>x</sub> concentrations on the inlet and outlet sides of respective NO<sub>x</sub> removal catalyst layers; NH<sub>3</sub> measurement means for determining NH<sub>3</sub> concentrations on the inlet and outlet sides of the same NO<sub>x</sub> removal catalyst layers; and percent NO<sub>x</sub> removal determination means for determining percent NO<sub>x</sub> removal ( $\eta$ ) on the basis of an inlet mole ratio (i.e., inlet NH<sub>3</sub>/inlet NO<sub>x</sub>). Therefore, the management unit detects an NO<sub>x</sub> removal catalyst layer that is actually deteriorated, whereby the deteriorated catalyst layer can be effectively replaced by a new catalyst layer.

#### Brief Description of the Drawings

[0029]

Fig. 1 schematically shows a configuration of a flue gas NO<sub>x</sub> removal apparatus equipped with an NO<sub>x</sub> removal catalyst management unit according to an embodiment of the present invention.

#### Best Modes for Carrying Out the Invention

[0030] Fig. 1 schematically shows a configuration of a flue gas NO<sub>x</sub> removal apparatus equipped with an NO<sub>x</sub> removal catalyst management unit according to an embodiment of the present invention. Actually, the flue gas NO<sub>x</sub> removal apparatus is provided in a thermal power station. However, no particular limitation is imposed on the facility that includes the NO<sub>x</sub> removal catalyst management unit of the embodiment.

[0031] As shown in Fig. 1, a flue gas NO<sub>x</sub> removal apparatus 10 includes an exhaust duct 12 and a treated gas duct 13. The exhaust duct 12 is in communication with a boiler unit installed in a thermal power station that is connected with an apparatus body 11 on the upstream side. The treated gas duct 13 is connected with the apparatus body 11 on the downstream side. In the apparatus body 11, a plurality of NO<sub>x</sub> removal catalyst layers (4 layers in this embodiment) 14A to 14D are disposed at predetermined intervals. The NO<sub>x</sub> removal catalyst layers 14A to 14D are arranged so that a discharge gas introduced through the exhaust duct 12 is sequentially passed therethrough, and reduce the level of nitrogen oxide (NO<sub>x</sub>) of the discharge gas through contact with the discharge gas passing through the catalyst layers. Notably, to the exhaust duct 12 communicating with the boiler unit, NH<sub>3</sub> is injected in an amount in accordance with the amount of the discharge gas fed from the boiler body.

[0032] No particular limitation is imposed on the type, shape, etc. of the catalysts 14A to 14D. Generally, each catalyst is composed of TiO<sub>2</sub> serving as a carrier and V<sub>2</sub>O<sub>5</sub> serving as an active component. The catalysts assume the form of honeycomb, plate, etc.

[0033] In the present embodiment, each catalyst layer employs a catalyst in the form of columnar honeycomb, and a plurality of catalyst layers are arranged in combination, thereby forming the catalyst layers 14A to 14D.

[0034] An NO<sub>x</sub> removal catalyst management unit 20 of the present embodiment is provided with gas sampling means 15A through 15E on the inlet and outlet sides of respective NO<sub>x</sub> removal catalyst layers 14A through 14D. The gas sampling means 15A through 15E are connected with NO<sub>x</sub> concentration measurement means 16A through 16E and with NH<sub>3</sub> concentration measurement means 17A through 17E. The data obtained by the measurement means are transferred to a percent NO<sub>x</sub> removal determination means 18 for calculating percent NO<sub>x</sub> removal and percent NO<sub>x</sub> removal contribution of the respective NO<sub>x</sub> removal catalyst layers 14A through 14D.

[0035] The gas sampling means 15A through 15E sample, via sampling tubes, a gas to be sampled in a desired amount and at a desired timing, and subsequently feed the sampled gas to the NO<sub>x</sub> concentration measurement means 16A through 16E and to the NH<sub>3</sub> concentration measurement means 17A through 17E. Notably, the sampling tubes and similar parts which are in contact with a gas to be sampled are required to be made of a material which has a predetermined heat resistance and which is inert to the corresponding gas. In the present embodiment, the gas sampling means 15A through 15E feed the sampled gas to the NO<sub>x</sub> concentration measurement means 16A through 16E and to the NH<sub>3</sub> concentration measurement means 17A through 17E. However, needless to say, each of the NO<sub>x</sub>

concentration measurement means 16A through 16E and the NH<sub>3</sub> concentration measurement means 17A through 17E may be provided with gas sampling means.

[0036] No particular limitation is imposed on the timing for sampling a gas by the gas sampling means 15A through 15E. Generally, sampling is carried out during usual operation of the power station, preferably at the nominal load where the amount of gas reaches the maximum, if possible. The interval between sampling operations may be prolonged to about six months, and the interval is sufficient for managing the performance of the NO<sub>x</sub> removal catalyst layers 14A through 14D. However, if the interval is shortened, precision in management is enhanced. Thus, the sampling is preferably carried out, for example, once every one to two months. Particularly, in a catalyst layer placed on the downstream side, variation of obtained data increases due to decrease in NH<sub>3</sub> concentration. Thus, in order to attain better management and evaluation, preferably, determination of NH<sub>3</sub> concentration is performed at short intervals, and percent NO<sub>x</sub> removal is calculated from an averaged NH<sub>3</sub> concentration value.

[0037] No particular limitation is imposed on the NO<sub>x</sub> concentration measurement means 16A through 16E and the NH<sub>3</sub> concentration measurement means 17A through 17E, so long as the measurement means can determine the NO<sub>x</sub> concentration measurement and the NH<sub>3</sub> concentration of the sample gas. Although an automated measuring apparatus is preferred, manual analysis means may also be employed. Needless to say, the NO<sub>x</sub> concentration and the NH<sub>3</sub> concentration may be directly determined by means of a sensor without sampling the gas.

[0038] As described above, the NO<sub>x</sub> concentration and the NH<sub>3</sub> concentration of the sampled gas are determined. In addition, oxygen or other components may also be determined, if required.

[0039] According to the present embodiment, NO<sub>x</sub> measurement means and NH<sub>3</sub> measurement means are provided on the inlet and outlet sides of respective NO<sub>x</sub> removal catalyst layers 14A through 14D. Alternatively, a single NO<sub>x</sub> concentration measurement means and a single NH<sub>3</sub> concentration measurement means are provided, and NO<sub>x</sub> concentrations and NH<sub>3</sub> concentrations on the inlet and outlet sides of respective NO<sub>x</sub> removal catalyst layers 14A through 14D may be analyzed sequentially. In this case, sampling of gas may be performed sequentially in accordance with measurement. Although time lags occur during sampling, they would not be any problem so long as the NO<sub>x</sub> removal operation proceeds consistently. However, it is preferred that sampling be simultaneously performed and the sampled gases be sequentially fed to the corresponding measurement means for analysis.

[0040] The percent NO<sub>x</sub> removal determination means 18 collects the measurement data from the NO<sub>x</sub> concentration measurement means 16A through 16E and the NH<sub>3</sub> concentration measurement means 17A through 17E, and calculates, from the measurement data, percent NO<sub>x</sub> removal and percent NO<sub>x</sub> removal contribution of respective NO<sub>x</sub> removal catalyst layers 14A through 14D. No particular limitation is imposed on the method of calculating percent NO<sub>x</sub> removal, and any method may be employed so long as the percent NO<sub>x</sub> removal is calculated on the basis of an inlet mole ratio (i.e., inlet NH<sub>3</sub>/inlet NO<sub>x</sub>) of the NO<sub>x</sub> removal catalyst layers 14A through 14D.

[0041] The reason for taking the inlet mole ratio into consideration is as follows. NH<sub>3</sub> is fed into an NO<sub>x</sub> removal apparatus in the vicinity of NO<sub>x</sub> removal catalysts on the upstream side in an amount proportional to that of the gas to be treated. The rate determining step of NO<sub>x</sub> removal reaction is a step of adsorbing NH<sub>3</sub> onto the catalysts. Therefore, it is most critical to detect NH<sub>3</sub> concentrations on the inlet and outlet sides of the NO<sub>x</sub> removal catalyst layers 14A through 14D upon management of the performance of the NO<sub>x</sub> removal catalyst layers 14A through 14D on the basis of NH<sub>3</sub> concentrations.

[0042] When calculated on the basis of an inlet mole ratio, the percent NO<sub>x</sub> removal may be calculated from NO<sub>x</sub> concentration or NH<sub>3</sub> concentration. However, NH<sub>3</sub>-basis calculation provides percent NO<sub>x</sub> removal values of higher precision suitable for management.

[0043] An exemplary procedure of deriving percent NO<sub>x</sub> removal will next be described. The percent NO<sub>x</sub> removal ( $\eta$ ) is determined on the basis of the following equation (2) employing NO<sub>x</sub> concentrations:

$$\eta = \{(\text{inlet NO}_x - \text{outlet NO}_x) / (\text{inlet NO}_x)\} \times 100 \times (\text{evaluation mole ratio} / \text{inlet mole ratio}) \quad (2).$$

[0044] As used herein, the term "evaluation mole ratio" refers to a mole ratio which is predetermined for the purpose of evaluating an NO<sub>x</sub> removal catalyst. The evaluation mole ratio may be predetermined to an arbitrary value; for example, 0.8, which is almost equal to a mole ratio typically employed for operating a power station.

[0045] Although the percent NO<sub>x</sub> removal ( $\eta$ ) is determined on the basis of the equation employing NO<sub>x</sub> concentrations, target catalysts can be evaluated on the basis of a percent NO<sub>x</sub> removal value actually reflecting the conditions of a catalyst, since the equation employs an inlet mole ratio. In general, since the percent NO<sub>x</sub> removal increases with NH<sub>3</sub>/NO<sub>x</sub>, the percent NO<sub>x</sub> removal must be derived on the basis of the inlet mole ratio so as to evaluate catalysts in an actual state.

[0046] The percent NO<sub>x</sub> removal ( $\eta$ ) is also determined on the basis of the following equation (1) employing NH<sub>3</sub>

concentrations:

$$\eta = \{(\text{inlet NH}_3 - \text{outlet NH}_3) / (\text{inlet NH}_3 - \text{outlet NH}_3 + \text{outlet NO}_x)\} \times 100 \times (\text{evaluation mole ratio} / \text{inlet mole ratio}) \quad (1).$$

[0047] Since the percent NO<sub>x</sub> removal (η) is determined on the basis of the equation employing NH<sub>3</sub> concentrations, variation in the obtained percent NO<sub>x</sub> removal values is smaller as compared with the case in which the equation employing NO<sub>x</sub> concentrations is used, which is advantageous. Thus, catalysts can be evaluated on the basis of percent removal values with smaller variation.

[0048] According to the present invention, percent NO<sub>x</sub> removal (η) of respective NO<sub>x</sub> removal catalyst layers 14A through 14D is determined through a technique on the basis of the inlet mole ratio, and the performance of the catalysts is managed on the basis of the determined percent NO<sub>x</sub> removal values. Specifically, when the percent NO<sub>x</sub> removal of a certain catalyst drops below a predetermined level, the catalyst having deteriorated performance undergoes performance restoration treatment. According to the invention, a catalyst which has been most deteriorated or a catalyst having a lowered percent NO<sub>x</sub> removal value below a predetermined level is exclusively subjected to performance restoration treatment. Therefore, NO<sub>x</sub> removal catalysts can be effectively used without performing unnecessary restoration treatment.

[0049] As used herein, the term "performance restoration treatment" generally refers to replacement of deteriorated catalysts with new catalysts, replacement of deteriorated catalysts with catalysts which have been regenerated by washing, or replacement of deteriorated catalysts with catalysts which have undergone regeneration treatment. Particularly when a honeycomb catalyst is used, a regenerated or un-regenerated NO<sub>x</sub> removal catalyst is placed such that the catalyst is inverted with respect to the direction of the flow of discharge gas, or a deteriorated NO<sub>x</sub> removal is replaced with a new NO<sub>x</sub> removal catalyst from which a deteriorated portion has been removed, whereby performance of the catalyst is restored. Notably, such restoration treatments are conceived on the basis of the finding of the present applicant that the upstream side of the discharge gas flow exclusively plays a great role in NO<sub>x</sub> removal reaction.

[0050] In the aforementioned embodiment, NO<sub>x</sub> removal catalysts of one flue gas NO<sub>x</sub> removal apparatus are managed by means of a single NO<sub>x</sub> removal catalyst management unit. Alternatively, NO<sub>x</sub> removal catalysts of a plurality of flue gas NO<sub>x</sub> removal apparatuses may also be managed by means of a single NO<sub>x</sub> removal catalyst management unit. Specifically, the percent NO<sub>x</sub> removal data obtained by the percent NO<sub>x</sub> removal determination means 18 may be transmitted in a wired or wireless manner to a central control system, whereby the percent NO<sub>x</sub> removal data are collectively controlled. Alternatively, concentration data obtained by NO<sub>x</sub> concentration measurement means 16A to 16E and NH<sub>3</sub> concentration measurement date 17A to 17E may be transmitted to a central control system, whereby the percent NO<sub>x</sub> removal data are collectively controlled. In any case, total performance evaluation of catalysts can be performed through collective management of a plurality of flue gas NO<sub>x</sub> removal apparatuses, thereby reliably attaining total management and effective performance management of NO<sub>x</sub> removal catalysts.

#### <Working Example>

[0051] Table 1 shows the results of NO<sub>x</sub> concentration measurement and NH<sub>3</sub> concentration measurement on the inlet and outlet sides of four respective NO<sub>x</sub> removal catalyst layers (similar to Fig. 1) of a flue gas NO<sub>x</sub> removal apparatus installed in an actual thermal power station. The measurement was carried out seven times: 1st (starting), 2nd (about 2 months after starting), 3rd (about 5 months after starting), 4th (about 7 months after starting), 5th (about 12 months after starting), 6th (about 24 months after starting), and 7th (about 30 months after starting).

[0052] As mentioned above, percent NO<sub>x</sub> removal on the basis of NO<sub>x</sub> concentration of each catalyst layer was calculated from measured NO<sub>x</sub> concentrations and NH<sub>3</sub> concentrations, and the results are shown in Table 2. Percent NO<sub>x</sub> removal on the basis of NH<sub>3</sub> concentrations of each catalyst layer was calculated in a similar manner, and the results are shown in Table 3.

[0053] Measurement was also performed with respect to the case where a portion of the second NO<sub>x</sub> removal catalyst layer had been replaced with a regenerated catalyst (regenerated by washing with water; having catalytic performance equivalent to that of an unused product, confirmed by a performance test). In a similar manner, NO<sub>x</sub> concentration and NH<sub>3</sub> concentration were measured on the inlet and outlet sides of the replaced portion of the second catalyst layer. The results are also shown in Table 1. In addition, percent NO<sub>x</sub> removal on the basis of NO<sub>x</sub> concentration of each catalyst layer was calculated from measured NO<sub>x</sub> concentrations and NH<sub>3</sub> concentrations, and percent NO<sub>x</sub> removal on the basis of NH<sub>3</sub> concentrations of each catalyst layer was calculated in a similar manner. The results are shown in Tables 2 and 3, respectively.

<Comparative Example>

[0054] Percent NO<sub>x</sub> removal and percent NO<sub>x</sub> removal contribution of each catalyst layer were calculated on the basis of the following equation (3):

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$$\eta = \{(\text{inlet NO}_x - \text{outlet NO}_x) / (\text{inlet NO}_x)\} \times 100 \quad (3),$$

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from NO<sub>x</sub> concentrations measured on the inlet and outlet sides of the catalyst layer in the Working Example. Table 4 shows the results. This technique is based on the method disclosed in Japanese Patent Publication (*kokoku*) No. 7-47108.

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[Table 1]

	Measurement	1st starting	2nd 2 months after	3rd 5 months after	4th 7 months after	5th 12 months after	6th 24 months after	7th 30 months after
NO <sub>x</sub> concentration (ppm)	1st layer inlet	148.7	166.6	208.3	228.1	221.6	166.7	175.9
	2nd layer inlet	65	72.3	85.7	111.4	94.4	78.8	78.9
	3rd layer inlet	44.6	46.4	44.7	51.8	48.6	47.6	44.0
	4th layer inlet	42.4	44.9	41.1	48.8	45.6	45.4	40.2
	4th layer outlet	39.4	39.4	36.9	44.2	43.3	42.3	38.0
	1st layer inlet	106.3	110.4	151.2	146.8	147.0	117.3	139.1
Ammonia concentration NH <sub>3</sub> (ppm)	2nd layer inlet	23.9	25.9	31.8	36.2	46.1	28.9	37.0
	3rd layer inlet	3	4	2.8	2.9	6.9	4.0	5.0
	4th layer inlet	3.2	2.2	2.3	1.8	5.4	3.0	2.0
	4th layer outlet	0.7	1.8	0.7	0.5	1.7	0.5	0.8
	2nd layer inlet	66.2	72.1	75.9	92.8	85.9	81.3	75.2
	2nd layer outlet	46.4	47.7	50.3	58.0	55.2	56.9	46.8
Regenerated layer (2nd layer) NO <sub>x</sub> concentration	2nd layer inlet	24.1	27.8	29.5	36.4	39.9	28.4	41.9
Ammonia concentration NH <sub>3</sub> (ppm)	2nd layer outlet	6.8	9.2	9.1	11.2	16.1	10.4	10.5



[Table 2]

	Measurement	1st starting	2nd 2 months after	3rd 5 months after	4th 7 months after	5th 12 months after	6th 24 months after	7th 30 months after
Reduced to mole ratio 0.8 NO <sub>x</sub>	1st layer	63.0%	68.3%	64.9%	63.6%	69.2%	59.9%	55.8%
	2nd layer	68.3%	80.0%	103.3%	131.8%	79.6%	86.5%	75.5%
	3rd layer	58.7%	30.0%	101.6%	81.5%	34.9%	42.7%	60.2%
	4th layer	75.0%	200.0%	147.6%	201.2%	33.1%	82.7%	90.9%
Regenerated layer (2nd layer)	NO <sub>x</sub>	65.7%	70.4%	69.3%	76.5%	61.5%	68.9%	54.3%

[Table 3]

	Measurement	1st starting	2nd 2 months after	3rd 5 months after	4th 7 months after	5th 12 months after	6th 24 months after	7th 30 months after
Reduced to mole ratio 0.8 NH <sub>3</sub>	1st layer	62.6%	65.1%	64.2%	61.9%	62.3%	60.1%	57.1%
	2nd layer	69.4%	71.6%	84.9%	96.3%	73.2%	75.1%	71.8%
	3rd layer	-5.6%	35.8%	15.7%	31.9%	18.1%	19.6%	49.7%
	4th layer	63.2%	16.4%	60.9%	63.6%	53.6%	66.5%	48.1%
Regenerated layer (2nd layer)	NH <sub>3</sub>	59.6%	58.2%	59.4%	61.8%	51.9%	55.1%	57.7%

[Table 4]

	Measurement	1st starting	2nd 2 months after	3rd 5 months after	4th 7 months after	5th 12 months after	6th 24 months after	7th 30 months after
Total percent NO <sub>x</sub> removal		73.5%	76.4%	82.3%	80.6%	80.4%	74.6%	78.4%
Percent contribution	1st layer	76.6%	74.1%	71.5%	63.4%	71.3%	70.7%	70.3%
	2nd layer	18.7%	20.4%	23.9%	32.4%	25.7%	25.1%	25.3%
	3rd layer	2.0%	1.2%	2.1%	1.6%	1.7%	1.7%	2.7%
	4th layer	2.7%	4.3%	2.5%	2.5%	1.2%	2.5%	1.6%
	Total	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%

## &lt;Performance evaluation&gt;

[0055] As is clear from Tables 1 to 4, percent NO<sub>x</sub> removal values of the third layer and the fourth layer calculated on the basis of only NO<sub>x</sub> concentrations (Comparative Example) are very small from the first measurement. The Test Example mentioned below has revealed that these small values do not reflect the actual states of the catalyst layers.

[0056] In contrast, according to the method of the Working Example employing mole ratios (NH<sub>3</sub>/NO<sub>x</sub>) (inlet mole ratio and evaluation mole ratio), percent NO<sub>x</sub> removal values on the basis of NH<sub>3</sub> concentrations and those on the basis of NO<sub>x</sub> concentrations were found to assess the actual states of the catalyst layers.

[0057] Through statistical processing of the data shown in Tables 2 and 3 of the Working Example so as to determine variation in a specific data set, percent NO<sub>x</sub> removal values calculated on the basis of NH<sub>3</sub> concentrations were found to have less variation. This was confirmed through the following procedure.

[0058] In the Working Example, since the evaluation mole ratio was set to 0.8, the theoretical percent NO<sub>x</sub> removal was 0 to 80% on the basis of the evaluation mole ratio. The incident of the values falling outside the above range was counted in Tables 2 and 3. Table 5 shows the results.

[0059] A simple average was calculated for percent NO<sub>x</sub> removal values obtained from the first measurement to seventh measurement shown in Tables 2 and 3, and the incident of the simple average values exceeding the theoretical percent NO<sub>x</sub> removal was counted. The results are shown in Table 6.

[0060] From the data in Tables 2 and 3, unbiased variance in percent NO<sub>x</sub> removal of each catalyst layer was calculated, and the obtained variance values were averaged. The percent NO<sub>x</sub> removal values falling outside the theoretical range were removed from the data shown in Tables 2 and 3, and approximate equations were derived from the remaining data through the least squares method. Pearson's product-moment correlation coefficients of the equations (r), r<sup>2</sup> (RSQ), and averaged values thereof were calculated. Table 7 shows the results.

[Table 5]

Catalyst layers	Outside the theoretical range	
	NH <sub>3</sub>	NO <sub>x</sub>
1st layer	0	0
2nd layer	2	3
3rd layer	1	2
4th layer	0	5
2nd layer (regenerated)	0	0
Total	3	10

[Table 6]

Catalyst layers	Average	
	NH <sub>3</sub>	NO <sub>x</sub>
1st layer	61.9%	63.5%
2nd layer	77.5%	89.3%
3rd layer	23.6%	58.5%
4th layer	53.2%	118.6%
2nd layer (regenerated)	57.7%	66.7%
Outside the theoretical range	0	2

[Table 7]

Catalyst layers	Variance		r <sup>2</sup> (RSQ)/least squares method	
	NH <sub>3</sub>	NO <sub>x</sub>	NH <sub>3</sub>	NO <sub>x</sub>
1st layer	0.0007	0.0022	0.812	0.537

[Table 7] (continued)

Catalyst layers	Variance		$r^2$ (RSQ)/least squares method	
	NH <sub>3</sub>	NO <sub>x</sub>	NH <sub>3</sub>	NO <sub>x</sub>
2nd layer	0.0094	0.0470	0.034	0.028
3rd layer	0.0310	0.0668	0.302	0.027
4th layer	0.0304	0.4260	0.031	0.168
2nd layer (regenerated)	0.0011	0.0050	0.167	0.351
Average	0.0145	0.1094	0.269	0.222

[0061] As is clear from Table 5, the incident of values falling outside the theoretical percent NO<sub>x</sub> removal range is larger in NO<sub>x</sub> than in NH<sub>3</sub>.

[0062] As is clear from Table 6, the incident of simple average values falling outside the theoretical percent NO<sub>x</sub> removal range is larger in NO<sub>x</sub> than in NH<sub>3</sub>.

[0063] As is clear from Table 7, variance in NO<sub>x</sub>-based percent NO<sub>x</sub> removal values is larger than variance in NH<sub>3</sub>-based percent NO<sub>x</sub> removal values. From Table 7, the averaged RSQ in relation to the least squares method is greater in the case of NH<sub>3</sub> than in the case of NO<sub>x</sub>, indicating that NH<sub>3</sub>-based percent NO<sub>x</sub> removal values have high correlation. In the cases of the fourth layer and the regenerated second layer, RSQ values are lower in the case of NH<sub>3</sub> than in the case of NO<sub>x</sub>. However, these values were obtained at unsatisfactory measurement precision, and the averaged correlation value is higher in the case of NH<sub>3</sub>. Therefore, NH<sub>3</sub>-basis data are concluded to have less variance.

[0064] As is clear from Tables 5 to 7, time-dependent change in percent NO<sub>x</sub> removal of each NO<sub>x</sub> removal catalyst layer is smaller in the case of NH<sub>3</sub>-concentration-basis percent NO<sub>x</sub> removal values than in the case of NO<sub>x</sub>-concentration-basis percent NO<sub>x</sub> removal values.

[0065] From the NH<sub>3</sub>-concentration-basis percent NO<sub>x</sub> removal values shown in Table 3, the percent NO<sub>x</sub> removal values falling outside the theoretical range were removed, and approximate equations were derived from the data falling within the theoretical range through the least squares method. On the basis of these approximate equations, percent NO<sub>x</sub> removal of each catalyst layer (12 months after the start of measurement) was calculated. Table 8 shows the results.

[Table 8]

Catalyst layers	5th (after 12 months)
1st layer	62%
2nd layer	74%
3rd layer	28%
4th layer	60%
2nd layer (regenerated)	58%

[0066] As is clear from Table 8, the most deteriorated NO<sub>x</sub> removal catalyst layer is estimated to be the third layer. At the fifth point in time of measurement, the degree of deterioration has been found to be in the sequence of the third layer, the regenerated second layer, the fourth and the first layers (approximately equal to each other), and the second layer.

[0067] In contrast, the results of the Comparative Example appear to indicate that the percent contribution of the first layer decreased and that of the second layer increased, thereby maintaining the performance of the NO<sub>x</sub> removal apparatus. That is, the first layer is concluded to be deteriorated.

<Test Example>

[0068] A portion of each of the catalyst layers employed in the Working Example was sampled, and the sample was evaluated in performance through the following method.

[0069] A portion (50 mm × 50 mm × 100 mm in length) was cut from the inlet side of the each NO<sub>x</sub> removal catalyst layer, and set in a performance test machine. The test gas was fed under the conditions which match the design values of an actual NO<sub>x</sub> removal apparatus, and percent NO<sub>x</sub> removal was determined by measuring NO<sub>x</sub> concentration and

NH<sub>3</sub> concentration on the outlet side of the catalyst sample. The results are shown in Table 9.

[0070] The results indicate a certain degree of deterioration of catalyst layers, and are almost identical to the aforementioned deterioration evaluation results.

[0071] As is clear from the above results, performance evaluation of NO<sub>x</sub> removal catalysts carried out in the Working Example reflects actual deterioration status; however, performance evaluation carried out in the Comparative Example does not coincide with actual performance evaluation.

[Table 9]

Catalyst layers	1st layer	2nd layer	3rd layer	4th layer	2nd layer (regenerated)
Percent NO <sub>x</sub> removal	78.5%	80.2%	69.1%	79.4%	77.7%
Order of deterioration	3	5	1	4	2

## 15 Claims

1. An NO<sub>x</sub> removal catalyst management unit for use with an NO<sub>x</sub> removal apparatus, the management unit being provided for managing a plurality of NO<sub>x</sub> removal catalyst layers provided in a flue gas NO<sub>x</sub> removal apparatus, **characterized in that** the management unit comprises NO<sub>x</sub> measurement means for determining NO<sub>x</sub> concentrations on the inlet and outlet sides of respective NO<sub>x</sub> removal catalyst layers; NH<sub>3</sub> measurement means for determining NH<sub>3</sub> concentrations on the inlet and outlet sides of the same NO<sub>x</sub> removal catalyst layers; and percent NO<sub>x</sub> removal determination means for determining percent NO<sub>x</sub> removal ( $\eta$ ) on the basis of an inlet mole ratio (i. e., inlet NH<sub>3</sub>/inlet NO<sub>x</sub>).
2. An NO<sub>x</sub> removal catalyst management unit according to claim 1 for use with an NO<sub>x</sub> removal apparatus, wherein the percent NO<sub>x</sub> removal ( $\eta$ ) is determined on the basis of NH<sub>3</sub> concentrations.
3. An NO<sub>x</sub> removal catalyst management unit according to claim 2 for use with an NO<sub>x</sub> removal apparatus, wherein the percent NO<sub>x</sub> removal ( $\eta$ ) is determined on the basis of the following equation (1):

$$\eta = \{(\text{inlet NH}_3 - \text{outlet NH}_3)/(\text{inlet NH}_3 - \text{outlet NH}_3 + \text{outlet NO}_x)\} \times 100 \times (\text{evaluation mole ratio/inlet mole ratio}) \quad (1).$$

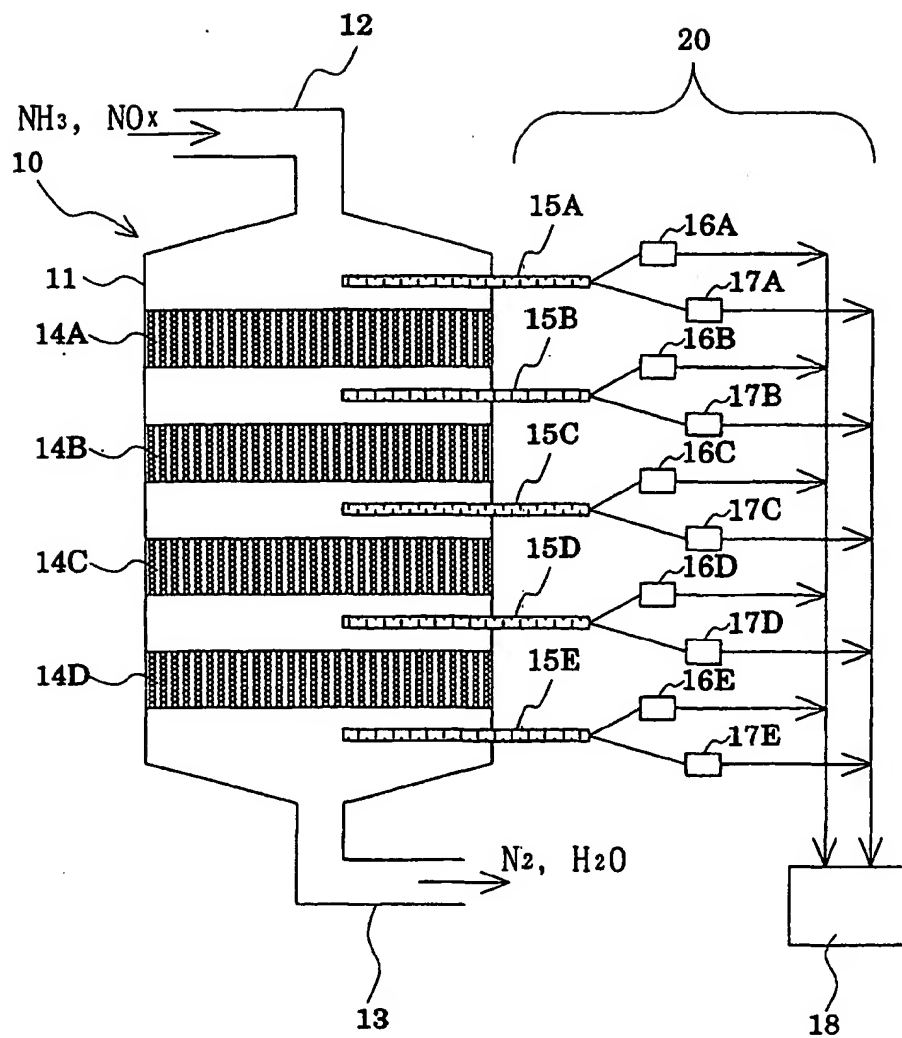
4. An NO<sub>x</sub> removal catalyst management unit according to any of claims 1 to 3 for use with an NO<sub>x</sub> removal apparatus, which management unit further includes transmission means for transmitting concentration values determined by the NO<sub>x</sub> measurement means and the NH<sub>3</sub> measurement means to the percent NO<sub>x</sub> removal determination means, wherein the percent NO<sub>x</sub> removal determination means determines the percent NO<sub>x</sub> removal ( $\eta$ ) of respective NO<sub>x</sub> removal catalyst layers included in a plurality of flue gas NO<sub>x</sub> removal apparatuses.
5. A method for managing an NO<sub>x</sub> removal catalyst for use with an NO<sub>x</sub> removal apparatus, the method being provided for managing a plurality of NO<sub>x</sub> removal catalyst layers provided in a flue gas NO<sub>x</sub> removal apparatus, **characterized in that** the method comprises determining NO<sub>x</sub> concentrations and NH<sub>3</sub> concentrations on the inlet and outlet sides of respective NO<sub>x</sub> removal catalyst layers; determining percent NO<sub>x</sub> removal ( $\eta$ ) on the basis of an inlet mole ratio (i.e., inlet NH<sub>3</sub>/inlet NO<sub>x</sub>); and evaluating performance of respective NO<sub>x</sub> removal catalyst layers on the basis of the percent NO<sub>x</sub> removal ( $\eta$ ).
6. A method according to claim 5 for managing an NO<sub>x</sub> removal catalyst for use with an NO<sub>x</sub> removal apparatus, wherein the percent NO<sub>x</sub> removal ( $\eta$ ) is determined on the basis of NH<sub>3</sub> concentrations.
7. A method according to claim 6 for managing an NO<sub>x</sub> removal catalyst for use with an NO<sub>x</sub> removal apparatus, wherein the percent NO<sub>x</sub> removal ( $\eta$ ) is determined on the basis of the following equation (1):

$$\eta = \{(\text{inlet NH}_3 - \text{outlet NH}_3)/(\text{inlet NH}_3 - \text{outlet NH}_3 + \text{outlet NO}_x)\} \times 100 \times (\text{evaluation mole ratio/inlet mole ratio}) \quad (1).$$

$$\text{NO}_x)) \times 100 \times (\text{evaluation mole ratio/inlet mole ratio}) \quad (1).$$

- 5 8. A method according to claim 5 for managing an NO<sub>x</sub> removal catalyst for use with an NO<sub>x</sub> removal apparatus, wherein the method further comprises performing restoration treatment of an NO<sub>x</sub> removal catalyst layer having a catalytic performance deteriorated to a predetermined level, on the basis of results of performance evaluation of the respective NO<sub>x</sub> removal catalyst layers.
- 10 9. A method according to claim 8 for managing an NO<sub>x</sub> removal catalyst for use with an NO<sub>x</sub> removal apparatus, wherein the performance restoration treatment is replacement of the NO<sub>x</sub> removal catalyst layer with a new NO<sub>x</sub> removal catalyst layer, replacement of the NO<sub>x</sub> removal catalyst layer with a regenerated NO<sub>x</sub> removal catalyst layer, replacement of the NO<sub>x</sub> removal catalyst layer with an NO<sub>x</sub> removal catalyst layer inverted with respect to the direction of the flow of discharge gas, or replacement the NO<sub>x</sub> removal catalyst layer with an NO<sub>x</sub> removal catalyst layer from which a deteriorated portion has been removed.
- 15 10. A method according to any of claims 5 to 7 for managing an NO<sub>x</sub> removal catalyst for use with an NO<sub>x</sub> removal apparatus, wherein the method further comprises determining the percent NO<sub>x</sub> removal of respective NO<sub>x</sub> removal catalyst layers included in a plurality of flue gas NO<sub>x</sub> removal apparatuses and evaluating catalytic performance of respective NO<sub>x</sub> removal catalyst layers included in a plurality of flue gas NO<sub>x</sub> removal apparatuses.
- 20 11. A method according to claim 8 for managing an NO<sub>x</sub> removal catalyst for use with an NO<sub>x</sub> removal apparatus, wherein the method further comprises determining the percent NO<sub>x</sub> removal of respective NO<sub>x</sub> removal catalyst layers included in a plurality of flue gas NO<sub>x</sub> removal apparatuses and evaluating catalytic performance of respective NO<sub>x</sub> removal catalyst layers included in a plurality of flue gas NO<sub>x</sub> removal apparatuses.
- 25 12. A method according to claim 9 for managing an NO<sub>x</sub> removal catalyst for use with an NO<sub>x</sub> removal apparatus, wherein the method further comprises determining the percent NO<sub>x</sub> removal of respective NO<sub>x</sub> removal catalyst layers included in a plurality of flue gas NO<sub>x</sub> removal apparatuses and evaluating catalytic performance of respective NO<sub>x</sub> removal catalyst layers included in a plurality of flue gas NO<sub>x</sub> removal apparatuses.
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FIG. 1



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP03/07538

A. CLASSIFICATION OF SUBJECT MATTER  
Int.Cl.<sup>7</sup> B01D53/94

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl.<sup>7</sup> B01D53/94, B01D53/86, B01D53/56

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1926-1996	Toroku Jitsuyo Shinan Koho	1994-2003
Kokai Jitsuyo Shinan Koho	1971-2003	Jitsuyo Shinan Toroku Koho	1996-2003

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	JP 7-47108 B2 (Kyushu Electric Power Co., Inc.), 24 May, 1995 (24.05.95), Claim 1; examples (Family: none)	1, 2, 4-6, 8-12 3, 7
Y A	JP 10-109018 A (Babcock-Hitachi Kabushiki Kaisha), 28 April, 1998 (28.04.98), Claims 2, 7; Par. No. [0007] (Family: none)	1, 2, 4-6, 8-12 3, 7

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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"Z" document member of the same patent family

Date of the actual completion of the international search  
26 August, 2003 (26.08.03)Date of mailing of the international search report  
09 September, 2003 (09.09.03)Name and mailing address of the ISA/  
Japanese Patent Office

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